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Life Testing of $Yb_{14}MnSb_{11}$ for High Performance Thermoelectric Couples

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Abstract. The goal of this study is to verify the long term stability of $Yb_{14}MnSb_{11}$ for high performance thermoelectric (TE) couples. Three main requirements need to be satisfied to ensure the long term stability of thermoelectric couples: 1) stable thermoelectric properties, 2) stable bonding interfaces, and 3) adequate sublimation suppression. The efficiency of the couple is primarily based on the thermoelectric properties of the materials selected for the couple. Therefore, these TE properties should exhibit minimal degradation during the operating period of the thermoelectric couples. The stability of the bonding is quantified by low contact resistances of the couple interfaces. In order to ensure high efficiency, the contact resistances of the bonding interfaces should be negligible. Sublimation suppression is important because the majority of thermoelectric materials used for power generation have peak figures of merit at temperatures where sublimation rates are high. Controlling sublimation is also essential to preserve the efficiency of the couple. During the course of this research, three different life tests were performed with $Yb_{14}MnSb_{11}$ coupons. TE properties of $Yb_{14}MnSb_{11}$ exhibited no degradation after 6 months of aging at 1273K, and the electrical contact resistance between a thin metallization layer and the $Yb_{14}MnSb_{11}$ remained negligible after 1500hr aging at 1273K. A sublimation suppression layer for $Yb_{14}MnSb_{11}$ was developed and demonstrated for more than 18 months with coupon testing at 1273K. These life test data indicate that thermoelectric elements based on $Yb_{14}MnSb_{11}$ are a promising technology for use in future high performance thermoelectric power generating couples.

Keywords: $Yb_{14}MnSb_{11}$, Thermoelectric couples, Sublimation suppression.

INTRODUCTION

New classes of thermoelectric materials have been extensively researched to develop thermoelectric devices with improved efficiencies [1-6]. Radioisotope Thermoelectric Generators (RTGs) are used on deep space missions where the limited solar fluxes at long distances from the sun make solar power impractical and mass constraints make chemical energy storage undesirable for the given power demand and mission duration. RTGs in earlier missions like Voyager and Cassini adopted Si-Ge thermoelectric couples. Although Si-Ge thermoelectric couples have demonstrated over 30 years of reliable operation in space, the desire for higher conversion efficiency to reduce the demand for Pu-238 and to increase the RTG specific power (W/kg) requires the development of more efficient thermoelectric materials. Zintl structure type materials such as $Yb_{14}MnSb_{11}$ [1] and rare-earth chalcogenides such as Lanthanum Telluride [2], and skutterudites such as cobalt antimonide [3,4] are some of the materials extensively researched to replace Si-Ge alloys for future RTGs. These materials show improved TE properties compared to Si-Ge, which increases efficiency, however, lifetime and reliability must be verified before these materials can be selected for use in support of future missions.

Stability of TE properties, sublimation suppression, and interfacial stability with the metallization layer are three main requirements to be verified with life testing. TE properties such as Seebeck coefficient, electrical resistivity and thermal conductivity are directly related to the efficiency of the couples and any degradation of these TE properties will lead to decreased power output. Protective sublimation barriers are also required to preserve the efficiency of thermoelectric devices and prevent contamination from sublimed materials during operation. The majority of thermoelectric materials for power generation operate at temperatures where sublimation rates are significant and can lead to increases in RTG internal resistances, degradation in thermal efficiency and short circuits. Therefore, the development of sublimation suppression methods is essential for long-lived thermoelectric power generating systems. Finally, stable interfaces are required for constructing and operating thermoelectric couples with long lifetimes. Negligible contact resistances during the entire lifetime are another important requirement to sustain the conversion efficiency of thermoelectric couples.

Life testing of $Yb_{14}MnSb_{11}$ material is the main focus of this study. $Yb_{14}MnSb_{11}$ exhibits a figure of merit exceeding 1 at 1273K [1] and is a promising candidate to replace p-type $Si_{0.8}Ge_{0.2}$ alloy. Lathanum telluride and skutterudites are also promising candidate materials for use in high efficiency thermoelectric couples, and life tests on these materials are in progress. For long term operation, lanthanum telluride is an n-type thermoelectric material with good thermal stability up to 1273K while p-type and n-type skutterudite are limited to temperatures up to 873K.

EXPERIMENTAL

A variety of coupons were prepared for life test. Coupon configurations were dependent upon which properties needed to be verified. For TE properties life tests, eliminating undesirable sublimation effects and test vessel contamination for the $Yb_{14}MnSb_{11}$ pucks during aging was the main focus. Graphite cups were machined to fit $Yb_{14}MnSb_{11}$ pucks and graphite plugs were also prepared to seal the graphite cups. Alumina paste was applied to bond graphite plugs and a cup in order to minimize the gap. These coupons were placed in a dynamic vacuum tube furnace ($<1\times10^{-5}$ Torr) and aged for 6 months at 1273K or 1323K. After aging, the coupon was taken out of the furnace and a slice was cut from the puck. TE properties were measured from the slice and compared with beginning of life values. The remaining puck was re-prepared in the same way and aged again. The Small ΔT Seebeck coefficient measurement system and the high temperature Hall effect system at the Jet Propulsion Laboratory (JPL) were used to measure Seebeck coefficient and electrical resistivity, respectively. Thermal conductivity was measured with a commercial thermal diffusivity system from Netsch (LFA 457 microflash). For sublimation life testing, different coupons were prepared. In order to expose the defined surface area, a non-reactive metallic clamp was incorporated to isolate the $Yb_{14}MnSb_{11}$ puck. Each puck was capped with graphite blocks with the same diameter and loaded in the clamps. Finally, the exposed surface of the coupons were coated with a thick alumina paste film (from Cotronics). The long term sublimation rates were calculated by measuring weight differences of the coupons after aging. Contact resistance coupons were prepared by bonding a metal layer between two $Yb_{14}MnSb_{11}$ pucks. Contact resistance of the coupons was measured with a 4 point probe set-up. One probe was fixed at one side of the coupon and the other probe moved across the coupon with a step size of approximately 100 micrometer, while a 1A current was applied through the coupon with the remaining two probes. Contact resistance values were obtained from the difference in the resistance values on either side of the metallization layer.

RESULT AND DISCUSSION

$Yb_{14}MnSb_{11}$ coupons maintain consistent TE properties after 6 months of aging at 1273K and 1323K in vacuum. Figure 1 compares TE properties of $Yb_{14}MnSb_{11}$ after 6 months aging with beginning of life values. The projected maximum operating temperature of $Yb_{14}MnSb_{11}$ is 1273K. An additional coupon was aged at 1323K as an accelerated life test. All three main transport properties (Seebeck coefficient, electrical resistivity, and thermal conductivity) showed little change after 6 months of aging and all the values were within ~ 10% of the baseline properties, which is within the typical measurement errors. Baselines were previously established from the measurements of multiple coupons synthesized from separate large batches of materials. This result indicates that there was no measurable change in any physical or electronic structure of $Yb_{14}MnSb_{11}$ after aging for 6 months at 1273K. Since all three thermoelectric properties of $Yb_{14}MnSb_{11}$ remained unchanged, the dimensionless figure of merit (zT) which is directly related to the efficiency of thermoelectric materials was preserved without any noticeable degradation (eq. 1).

$$zT = \frac{\alpha^2 \sigma}{\kappa} T \tag{1}$$

where α is the Seebeck coefficient, σ is the electrical conductivity, κ is the thermal conductivity, and T is the absolute temperature.

Sublimation is one of the main degradation mechanisms in some of thermoelectric materials and sublimation suppression schemes need to be evaluated or developed for each thermoelectric material. Figure 2 lists beginning of life sublimation rates of several TE materials at the projected operating temperature. Si-rich Si-Ge is one of the thermoelectric materials adopted in earlier RTGs and a silicon nitride coating [7] was incorporated as a sublimation suppression layer. As shown in Figure 2, $Yb_{14}MnSb_{11}$ exhibits a sublimation rate 100 times higher than $Si_{0.8}Ge_{0.2}$ at the beginning of life.

Sublimation barriers have a couple of basic requirements, and the development of new barriers becomes more complicated as sublimation rates increase. The first requirement is stability, which includes temperature stability and chemical stability of the thermoelectric materials. The second is to withstand stress during thermal cycling. The protective layers should either have a similar coefficient of thermal expansion (CTE) as the thermoelectric materials or withstand stresses from thermal cycling. A LPCVD (Low Pressure Chemical Vapor Deposition) silicon nitride layer is a suitable sublimation layer for Si-Ge because there is no significant reaction between silicon nitride and Si-Ge at the operating temperature and stresses in a deposited silicon nitride layer can be minimized by controlling deposition parameters.

Since $Yb_{14}MnSb_{11}$ is quite different than SiGe in terms of chemistry and possesses a large CTE, new approaches need to be taken for the development of a sublimation suppression layer. The first challenge is that only a few materials are compatible with $Yb_{14}MnSb_{11}$ at 1273K. Antimony is prone to react with most metals and ytterbium has a strong affinity for oxygen and reduces most oxides. After extensive screening tests, only a few materials showed limited reactivity with $Yb_{14}MnSb_{11}$ including refractory metals such as molybdenum [8], as well as aluminum oxide and graphite. The second challenge is that all of those candidates exhibit CTE values much lower than that of $Yb_{14}MnSb_{11}$. One way to alleviate the problem of CTE discrepancy is to keep the protective layer thin. However, the relatively high sublimation rates of $Yb_{14}MnSb_{11}$ make it difficult to use any thin film as a sublimation suppression layer. A sublimation suppression layer can delaminate from the substrate by under cutting from any defects and the amount of under cutting is proportional to the sublimation rate. Several thin films were investigated, but all the deposited layers delaminated from $Yb_{14}MnSb_{11}$ within a few weeks. Since the chemical stability with $Yb_{14}MnSb_{11}$ is the most crucial requirement, the focus was to find a way to process initial candidates to maintain adhesion to $Yb_{14}MnSb_{11}$. One approach was to incorporate a porous layer rather than a dense layer. Porous layers are more flexible and can withstand the stresses from CTE differentials. Commercial alumina paste (from Cotronics) was adopted to deposit a porous alumina layer.

Figure 3 exhibits sublimation test results from $Yb_{14}MnSb_{11}$ coupons with an alumina paste layer. Sublimation rates of $Yb_{14}MnSb_{11}$ decreased ~1000 times at 1273K with the alumina paste layer [9]. Initial sublimation rates of the coupon were $\sim 3\times10^{-5}$ g·cm^2/hr and the rate decreased with time and settled at $\sim 2\times10^{-6}$ g·cm^2/hr after 1500 hrs. Subsequently, the sublimation rates of the coupons displayed the same level for the next 18 months. Based on these data, the sublimation kinetics is projected to remain stable over the full 15 years of desired operation. During the test, sublimation rates were obtained by cooling down the coupons and measuring the weight every 1~4 weeks. The alumina paste layer was able to withstand stresses from numerous thermal cycles and stayed in contact with the $Yb_{14}MnSb_{11}$. In order to determine an acceptable sublimation rate, a sublimation suppression goal was calculated based on ~ 10% cross section reduction at the hot end of the thermoelectric leg after 14 years of operation and the value for $Yb_{14}MnSb_{11}$ was $\sim 2\times10^{-6}$ g·cm^2/hr at 1273K. The sublimation rate of the $Yb_{14}MnSb_{11}$ coupon with alumina paste layer met the sublimation goal at 1273K.

Alumina paste layer serves as an excellent sublimation suppression barrier for $Yb_{14}MnSb_{11}$ because alumina paste layer gets naturally dense through clogging with ytterbium oxide during operation. Although alumina paste was adopted due to its unique compatibility with $Yb_{14}MnSb_{11}$, the porous structure of alumina paste layer has limitations on suppressing sublimation. As shown in Figure 3, initial sublimation rates were more than 10 times higher than the sublimation suppression goal. However, the sublimation rate decreased with time and eventually met the goal. Ytterbium has an extremely strong affinity to oxygen and is oxidized even in high vacuum ($< 10^{-5}$ Torr). When sublimed from the surface of $Yb_{14}MnSb_{11}$, ytterbium was oxidized while passing through the tortuous porous structure of alumina paste. When ytterbium oxide is formed, pores in the alumina paste are clogged and sublimation rates decreases.

Figure 4 confirms that alumina paste layer is clogged with ytterbium oxide during sublimation of $Yb_{14}MnSb_{11}$. Figure 4(a) is a SEM picture of the hot end (~ 1273K) of a $Yb_{14}MnSb_{11}$ sublimation coupon aged in-gradient for 1500 hr in vacuum and Figure 4(b) is a SEM picture of the cold end (~773K) of the coupon. At 773K, there is no measurable sublimation from $Yb_{14}MnSb_{11}$ and the alumina paste layer remains unchanged. At 1273K, ytterbium and antimony sublimes from $Yb_{14}MnSb_{11}$. Antimony passes through the porous structure of alumina paste layer, however, ytterbium is oxidized during sublimation through the porous structure and the pores in the alumina paste layer get clogged. Alumina paste layer clogged with ytterbium oxide is clearly observed in Figure 4(a). As clogging proceeds, even the passage of antimony through the alumina paste layer is suppressed and the overall sublimation rate decreases.

Figure 5 illustrates that negligible contact resistance was measured on a $Yb_{14}MnSb_{11}$/Mo/$Yb_{14}MnSb_{11}$ coupon after 1500hr of aging at 1273K in vacuum. The location of the Mo layer is indicated on the graph and there was no change in the resistance value when the probe passed through the interface. This result indicates that the bonding between Mo and $Yb_{14}MnSb_{11}$ is preserved during aging and the Mo layer can be used as a metallization layer when constructing thermoelectric couples with $Yb_{14}MnSb_{11}$.

CONCLUSION

Three different life tests have been conducted with $Yb_{14}MnSb_{11}$ and life test results successfully demonstrated that $Yb_{14}MnSb_{11}$ remains stable and can be incorporated into high efficiency thermoelectric couples. TE property life tests verified that thermoelectric properties of $Yb_{14}MnSb_{11}$were stable after 6 months of aging at both 1273K and 1323K. Thermoelectric couples for RTGs must typically operate more than 14 years, and aging and testing of coupons is continuing as further verification. TE property life tests exhibited very promising initial results. Another important achievement during this research was the development of a stable sublimation suppression layer for $Yb_{14}MnSb_{11}$. Since $Yb_{14}MnSb_{11}$ exhibited different sublimation behavior compared with Si-Ge alloy, a new approach was taken for the development of a sublimation suppression layer. The porous alumina layer accommodated stresses from the CTE discrepancy and stayed intact with the $Yb_{14}MnSb_{11}$. Although initial sublimation rates were higher than the goal because of the porous structure of alumina paste layer, the sublimation rates decreased with time as pores became clogged with ytterbium oxide which is a natural by-product of $Yb_{14}MnSb_{11}$ sublimation. The sublimation suppression goal was calculated assuming a 10% cross section reduction at the hot end of the leg in the potential thermoelectric devices and the sublimation rate of $Yb_{14}MnSb_{11}$ with alumina paste layer continued to decrease and finally met the goal after 1500 hr aging at 1273K. More importantly, the sublimation rate stayed at the same level and continued to meet the goal for the next 18 months, and it is reasonable to project that these rates would remain low for the full life of an RTG. Final life tests should verify stable bonding between the Mo metallization layer and $Yb_{14}MnSb_{11}$. Although only limited tests have been conducted to date, the contact resistance between the Mo metallization layer and the $Yb_{14}MnSb_{11}$ remained negligible after 1500 hr of aging at 1273K.

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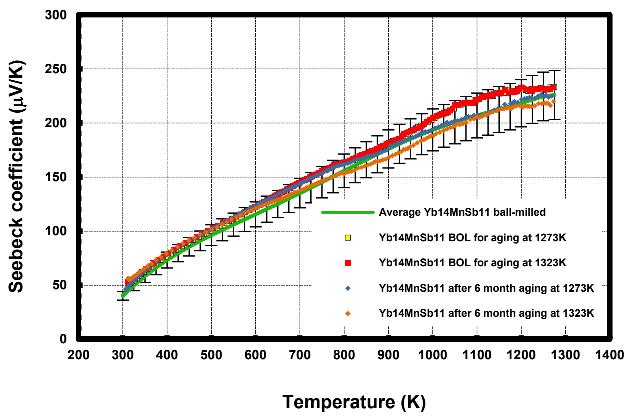
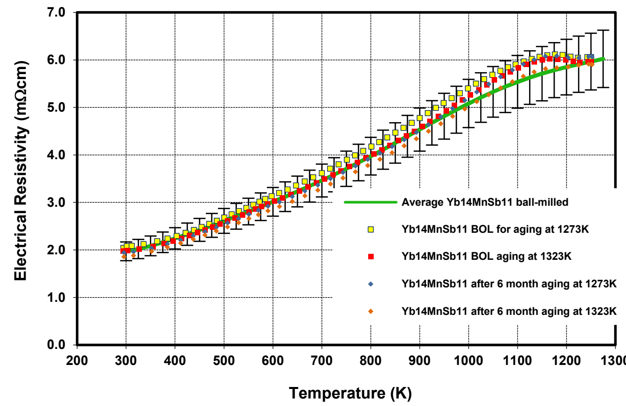


(a)



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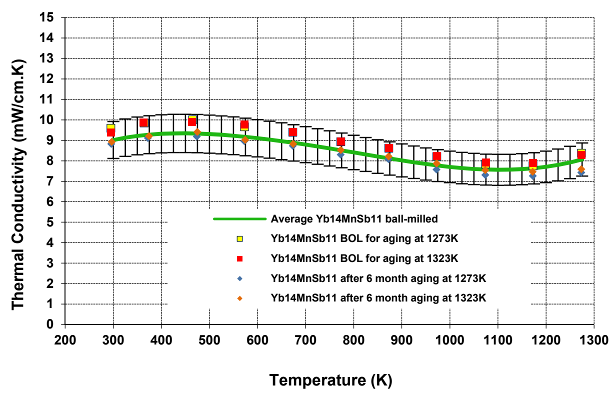
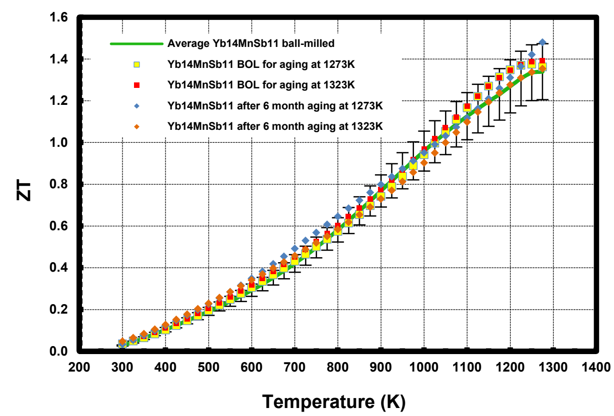


(c)



(d)

FIGURE 1. Thermoelectric properties life test results with $Yb_{14}MnSb_{11}$:(a) Seebeck coefficient, (b) electrical resistivity, (c) thermal conductivity, and (d) dimensionless figure of merit as a function of temperature and aging time; (BOL: Beginning-of-life).

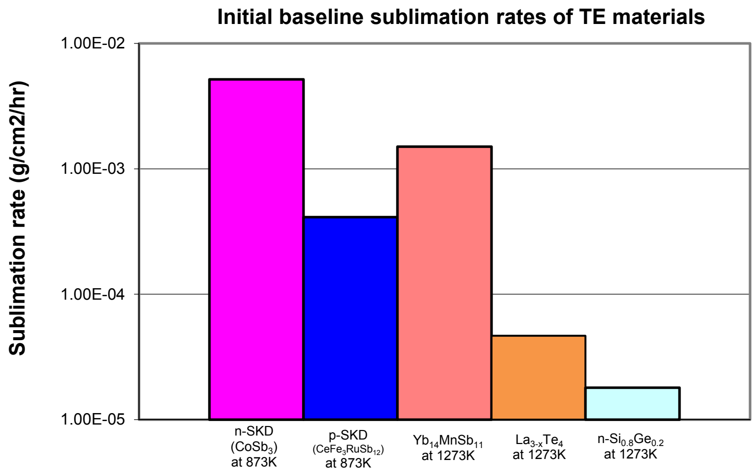


FIGURE 2. Beginning of life (BOL) sublimation rates of various thermoelectric materials under dynamic vacuum (bare coupons without sublimation suppression coatings)

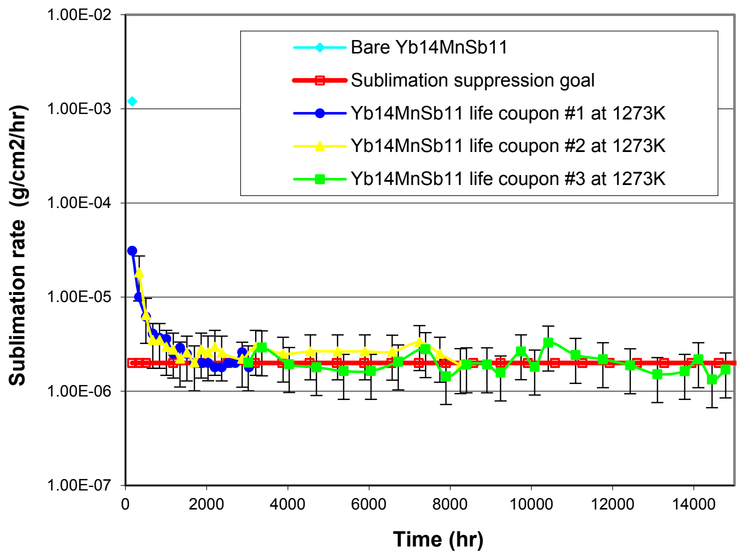
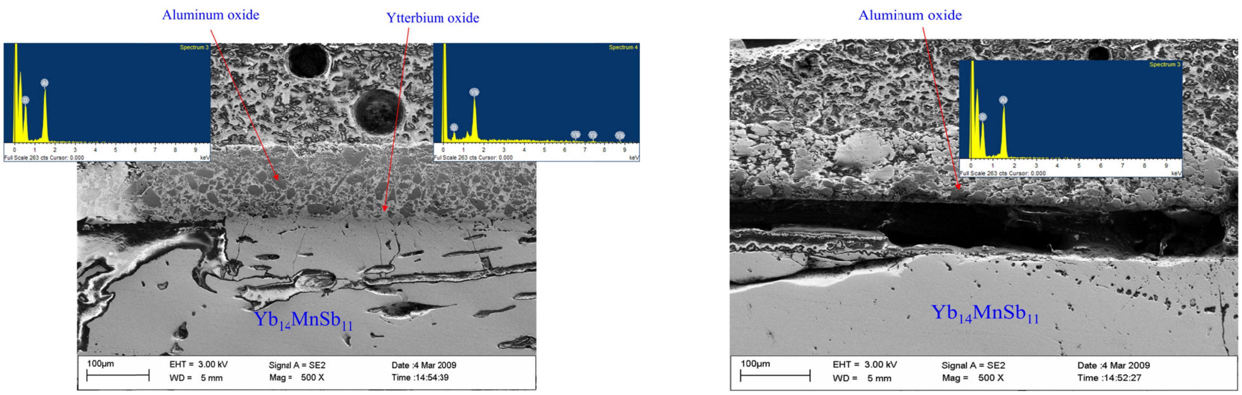


FIGURE 3. Sublimation life test result from $Yb_{14}MnSb_{11}$ coupons with sublimation suppression coatings (alumina paste layer) at 1273K under dynamic vacuum.



(a) (b)

FIGURE 4. Cross section SEM images of a $Yb_{14}MnSb_{11}$ coupon with sublimation suppression coating (alumina paste layer) aged in-gradient for 1500 hr under dynamic vacuum ((a) the hot end of the coupon: ~ 1273K, (b) the cold end of the coupon : ~ 773K)

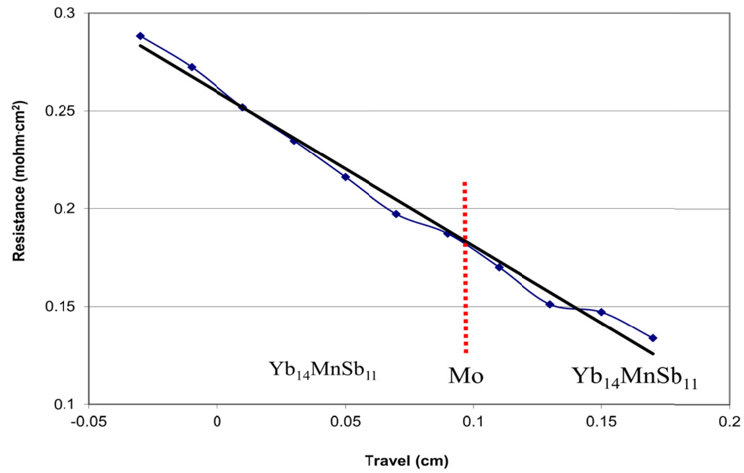


FIGURE 5. Electrical contact resistance measurement of a $Yb_{14}MnSb_{11}$/Mo/ $Yb_{14}MnSb_{11}$ coupon after 1500 hr aging at 1273K under dynamic vacuum. Results demonstrate that contact resistances remain negligible and that Mo-based metallization layers are a good candidate for long life high temperature couples.